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Spatial distribution of LiNbO₃ single crystals optical properties changes after redox high-temperature treatment

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The changes in optical properties of bulk LiNbO₃ crystals were investigated depending on the diffusion depth. For this purpose the samples were isochronously annealed in hydrogen, subsequently the reduced samples were isochronously annealed in air. The investigations were held in different crystallographic directions. The experimentally determined distribution of depth-dependent additional absorption in reduced crystals was approximated basing on the oxygen vacancies diffusion model and solution of differential equations set describing the quasichemical reaction of bipolarons formation due to the oxygen loss in LiNbO₃ crystal.

1. Introduction

High temperature annealing of lithium niobate (LiNbO₃, LN) in vacuum, reducing and oxidizing environments, in the presence of metal ions, in proton-rich liquids etc is one of the techniques, which is extensively used to create LN-based elements for acoustoelectronics, optoelectronics and integrated optics [1-3]. However such thermochemical treatments alter the optical and electrical properties of LN. These changes are based on ions diffusion processes out of the crystal into the environment and vice versa, that affect the chemical composition of LN and its defect subsystem state. The diffusion processes in LiNbO₃ are studied in a significant amount of works, for example [4-13].

Since in most cases diffusion surface layers with several microns thickness are sufficient for practical applications, the changes in chemical composition of LN layers in depth (and, consequently, changes in their properties) caused by the diffusion processes, are mainly studied by mass spectroscopy of secondary ions (SIMS) (see. e.g. [5]). This technique allows determining the changes only in micron-range and the measurements are performed in the direction of diffusion. Only in [6, 7] the changes in the optical properties of bulk congruent LN samples with about 3 mm thickness, treated by VTE technique, were investigated by means of second harmonic generation conditions analysis and spectrometry in the direction, perpendicular to the direction of diffusion.

Therefore the targeted investigations of coloration changes in LN crystals, caused by redox annealing, depending on the distance from crystals surface (for a few millimeters deep into the crystal) were not performed. Thereby it is not known how the coloration processes occur at different temperatures in crystals volume during redox treatment.

Furthermore, the diffusion mechanisms during thermochemical treatments are also not completely clear. In [8] it is considered that the main diffusion mechanism in congruent LiNbO₃, which contains no impurity ions, is the diffusion of lithium and lithium vacancies. In [9] it is assumed that both lithium and niobium diffusion processes take place simultaneously. Authors in [10, 11] consider the oxygen diffusion as the main mechanism and in [4, 12] – the diffusion of oxygen and lithium. Moreover, the known data about anisotropy of the diffusion processes is also controversial. For example in [3] the lithium diffusion is considered as isotropic, however in [13] it is assumed that the lithium diffusion coefficient in Y-direction is greater than in Z-direction. Thus, despite the fact that understanding of the diffusion mechanisms during thermochemical treatments in nominally undoped LN is vital for determining the nature of changes in the crystals, the results of existing works are contradictory. Therefore the aim of this work is the investigation of changes in optical properties with the depth of diffusion in different crystallographic directions of bulk LiNbO₃ crystals under the influence of

isochronous annealing in H₂ and subsequent isochronous annealing of reduced samples in air. The mathematical simulation for the obtained dependences of properties changes is proposed.

2. Experimental details

All investigated samples were cut from the congruent LN crystals, grown at SRC “Carat” [14]. The samples with dimensions 7(X)×15(Y)×32(Z) mm were sealed in ampoules, filled in with pure H₂ (pressure 0.5 bar at room temperature) and then annealed for 1 our at 400, 500, 600 and 700 °C. The hydrogen was chosen due to the fact that coloration occurs most effectively in this case and additional absorption spectrum has in general a similar structure and nature as after annealing in vacuum.

Five samples, annealed in H₂ at 600 °C were chosen for further treatment in air for 1 hour at 400, 500, 525, 550 and 600 °C respectively. In all cases the heating rate was 5 K / min.

Absorption spectra of the samples after annealing were investigated on UV3600 Shimadzu spectrophotometer (Japan) in the 300-800 nm region with the specially designed device, which allowed scanning by light beam with 150 μm step through the aperture with 100 μm in diameter, and studying the coloring changes with thickness in X, Y, Z directions.

The scheme of crystal cutting after annealing and scan directions of the obtained plates is shown in Fig.1. The cut plates were then polished to the thickness of 1 mm.

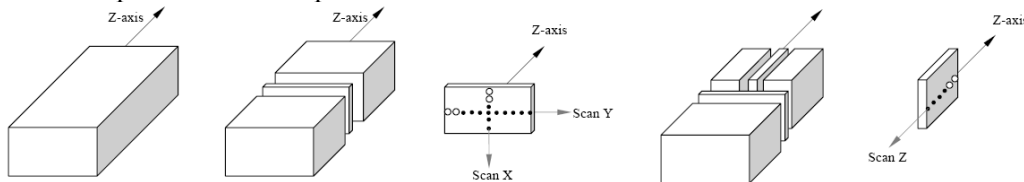


Fig.1. Scheme of the cutting of annealed samples and scan directions of the obtained plates

The changes in structural parameters of reduced LN crystals were determined by the XRD technique on the DRON-3 (Russia) diffractometer in the reflection mode. The comparative studies of the sample surfaces, which were in direct contact with annealing environment and those, which were obtained after cutting from the inner part of the annealed crystal have been performed.

3. Results and discussion

3.1. Annealing in H₂

After annealing in H₂ at 400 °C the uncut samples have dark brown color, after annealing at higher temperatures they become completely opaque. However, this is only an illusion. The coloration is maximal near the surfaces, which were in contact with the annealing environment and gradually decreases as it approaches the center of the crystal. Even after annealing at 700 °C the center of the crystal remains transparent. To characterize the coloration changes depending on the distance from the surface the additional absorption spectra (AA) ΔK were determined at each scan point according to $\Delta K = \frac{1}{d} \ln \frac{T_n}{T_c}$, where d is the thickness of the sample, T_n is the transmission of the sample in the n point,

T_c is the transmission in the middle of the sample. In general for X, Y, Z directions and for all studied annealing temperatures it can be assumed that AA spectrum is a superposition of three bands with maxima in the regions of 350-410, 500-520 and 700-750 nm. The relative contribution of these bands to the AA is different and depends on the distance from the surface to the point where the spectrum has been recorded and on the annealing temperature (Fig. 2). The difference in the position of the AA maxima is also observed depending on the crystallographic direction. For example, AA spectra, registered at different points of crystal (scanning along Z – axis) after annealing at different temperatures are shown in Fig. 2. As it can be seen from Fig. 2 the shortwave band prevails in the spectrum after annealing at 400 °C. However after annealing at 500 °C the band with the maximum at 500-520 nm is predominant. It is necessary to note that authors in [15] have also observed the similar difference in spectra after reducing annealing of thin LN plates in vacuum. After annealing at 700 °C the absorption

in the short-wave region prevails in an area, which is adjacent to the sample surface. Besides the shortwave band and the band with the maximum at 500 nm, the band with the maximum at 700-750 nm is clearly evident in spectrum. Its intensity decreases with the distance from the sample surface and the intensities of the shortwave band and 500 nm band become comparable.

Anisotropy of coloration is illustrated in Fig. 3, which shows the AA change at 510 nm depending on depth along X , Y , Z directions after annealing at 700 °C. The deepest coloration is observed in Z -direction to a distance of about 10 mm from the sample surface; in Y -direction the coloration depth is about 6 mm and in X -direction – 4 mm. These differences are apparently related to the crystal structure – along the third order axis of symmetry (Z -direction) there are so-called "channels" that are likely to facilitate the movement of ions in the LiNbO_3 lattice. The dependence of the absorption changes with depth is similar also at other wavelengths.

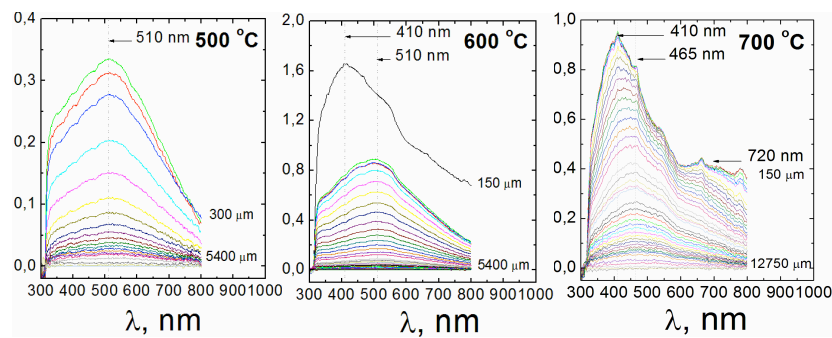


Fig.2. Additional absorption ΔK (see above) spectra of LN after annealing in H_2 at different T and different depths from the surface (scanning along Z -direction).

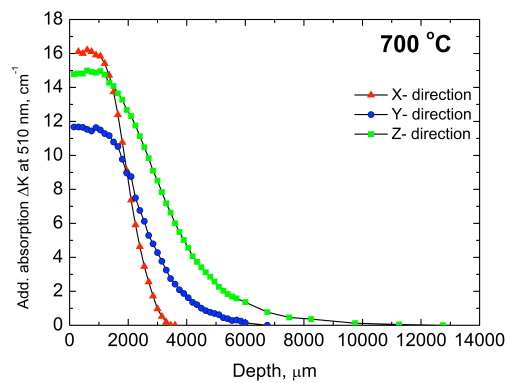


Fig. 3. Change of additional absorption ΔK at $\lambda = 510$ nm in LN depending on depth along X , Y , Z directions after annealing in H_2 at 700 °C. Dots - experimental data, solid lines – approximation (see text for details).

X-ray studies of the LN sample show that after annealing in H_2 at 700 °C the crystal structure of the surface, which has been in direct contact with the annealing environment changed (see Fig. 4). Observed reflections correspond to phase LiNb_3O_8 , which is compared with LiNbO_3 depleted Li, according to the ICDD database. The thickness of the LiNb_3O_8 layer estimated from the X-ray extinction coefficient is not lower than 25 μm .

3.2. Annealing in air after high temperature H_2 -treatment

Oxidizing annealing of LN samples that were previously annealed in H_2 at 600 °C leads to discoloration crystals. The sample plates, cut from the crystals, which were annealed at different temperatures, are shown in Fig. 5. The transparent area with a thickness of less than 100 μm appears near the

crystal surface after it was heated to 400 °C. In the temperature range of 500-550 °C the discoloration process occurs more intensively and at 600 °C the sample is almost transparent.

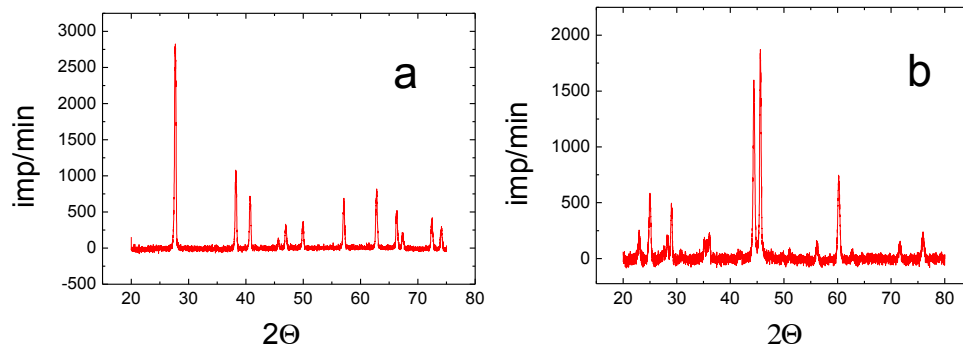


Fig. 4. Diffraction patterns of LN surfaces after annealing in H_2 at 700 °C: *a* – internal surface of the cut sample, $LiNbO_3$ phase; *b* – surface, which was in contact with environment, $LiNb_3O_8$ phase.

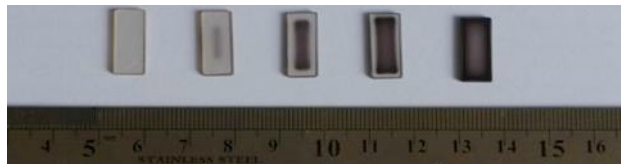


Fig. 5. The plates, cut from the crystals, which were previously annealed in H_2 at 600 °C and subsequently annealed in air at 400, 500, 525, 550, 600 °C (the plates are arranged gradually depending on the temperature, the right plate corresponds to 400 °C and the left – to 600 °C)

Thin transparent layer of the sample, treated at 400 °C does not allow measuring the absorption changes with depth by the above described method. Investigations of samples that were annealed at higher temperatures show that absorption in each of the selected spectral range (350-410, 500-520 and 700-750 nm) has the maximum and its position shifts deep into the crystal with the increase of the annealing temperature. As an example, the changes of AA along Z-direction are shown in Fig. 6. The changes were registered at 510 nm after air annealing at 525 °C and 550 °C.

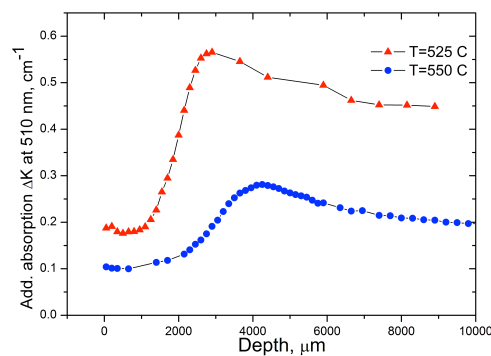


Fig. 6. Changes of additional absorption of LN along Z-axis ($\lambda=510$ nm) after air annealing at 525 and 550 °C

3.3. Mathematical description of the $LiNbO_3$ coloration change under redox treatment

As it is seen from the aforementioned results, as well as from the results, obtained previously in the *in situ* mode [16], observed coloration changes caused by change of annealing atmosphere from reducing to oxidizing and vice versa are reversible. Thus, it can be assumed that the oxygen in- and

out-diffusion processes underlie the coloration/discoloration mechanisms in LiNbO₃ crystals. The model, which were used to describe the depth dependent coloration changes in LN after redox annealing, bases on the following key assumptions: (i) the oxygen diffusion occurs according to the vacancy mechanism; (ii) vacancy (V_O) in-diffusion during reduction leads to the formation of new defects that increases the optical absorption of the crystal; (iii) the defects formation process can be described as the quasi-chemical reaction of the second order.

These assumptions were used to describe the depth distribution of AA at 510 nm, which occurs in LN after reducing at 700 °C (Fig. 3). Most authors, who have studied the optical properties of reduced LN, connect this absorption band with bipolarons formation (bound pair: Nb⁴⁺ in a regular structural position – Nb⁴⁺ in the position of Li). Initially the defects, which are formed as the result of oxygen vacancies diffusion to crystal are bound polarons (Nb⁴⁺ in the structural position of Li) [16, 17], and the formation of bipolarons on their basis is considered to occur instantly for simplification.

The V_O diffusion is described by the second Fick's law:

$$\frac{\partial n_v}{\partial t} = D \frac{\partial^2 n_v}{\partial^2 x}, \quad (1)$$

where n_v is the V_O concentration, D is the diffusion coefficient, x is the distance from the crystal surface in the diffusion direction and t is the annealing time.

On the crystal surface the boundary conditions of the third order are applied:

$$-D \frac{\partial n_v}{\partial \vec{n}} = R (n_v - N_{vf}), \quad (2)$$

where R is the oxygen mass transfer coefficient from the crystal to the environment, N_{vf} is the equilibrium V_O concentration after annealing, \vec{n} is the internal normal to the surface.

The reaction of bound polarons formation can be written as following:



where V denotes an oxygen vacancy, X is the niobium ion in lithium position Nb_{Li}, Y is the bound polaron.

The velocities of the direct and inverse reactions of bound polarons n_y concentration change can be written according to (3) as:

$$\frac{\partial n_y}{\partial t} = -\frac{\partial n_x}{\partial t} = k_f n_v n_x, \quad -\frac{\partial n_y}{\partial t} = \frac{\partial n_x}{\partial t} = k_b n_y, \quad (4)$$

where n_x is the concentration of Nb_{Li}⁵⁺ ions, k_f та k_b are the velocity constants of the direct and inverse reactions in (3). Considering the processes of diffusion and formation/destruction of bound polarons, one gets a set of differential equations:

$$\begin{cases} \frac{\partial n_v}{\partial t} = D \frac{\partial^2 n_v}{\partial^2 x} - k_f n_v n_x + k_b n_y, \\ \frac{\partial n_x}{\partial t} = -k_f n_v n_x - k_b n_y, \\ \frac{\partial n_y}{\partial t} = k_f n_v n_x - k_b n_y. \end{cases} \quad (5)$$

To simplify the calculations, all concentrations were normalized on the total concentration of Nb_{Li} ions $N_0 = n_x + n_y$.

Determining of $n_y(x)$ from (4) allows calculation of the absorption change by the formula:

$$A(x) = k_c n_y(x), \quad (6)$$

where k_c is the proportionality factor.

Approximation of experimental dependencies was made basing on (6) by the Levenberg-Marquardt method with the following parameters of approximation: D , R , k_f , k_b , k_c , N_{v0} , N_{vf} (N_{v0} – V_O concentration before annealing). The approximation results for different crystallographic directions are given in Fig. 3 (solid lines) and the obtained values of fitting parameters are indicated in Table 1. As seen from Fig. 3, the results of approximation are satisfactory. Obtained dependences of AA change

caused by reducing annealing allowed calculation of V_O diffusion coefficients in X , Y , Z directions: $D_x = 3 \cdot 10^{-6}$, $D_y = 7 \cdot 10^{-6}$, $D_z = 1,2 \cdot 10^{-5}$ cm²/s. This result confirms the anisotropy of diffusion processes caused by the peculiarities of the LiNbO₃ structure.

Approximation of coloration change curves during oxidation annealing of previously reduced crystals using the same model did not allow obtaining an adequate fit. This may be caused by the fact that the process of oxidation is more complicated due to the lithium loss during the reduction processes and due to the oxygen diffusion from the areas of the crystals, which were not reduced.

Table 1. The obtained values of fitting parameters

Direction	$D, 10^{-6}$ cm ² /s	$R, \text{cm/s}$	$k_f \cdot N_0, \text{s}^{-1}$	k_b, s^{-1}	$k_c \cdot N_0, \text{cm}^{-1}$	N_{v0}/N_0	N_{vf}/N_0
x	3	0.17	$5.4 \cdot 10^{-4}$	$2.7 \cdot 10^{-4}$	17.2	$2 \cdot 10^{-13}$	13.0
y	7	0.17	$1.9 \cdot 10^{-4}$	$4 \cdot 10^{-10}$	11.8	$5 \cdot 10^{-8}$	13.0
z	12	0.17	$1.3 \cdot 10^{-4}$	$8 \cdot 10^{-11}$	15.2	$1 \cdot 10^{-8}$	13.0

4. Conclusions

Observed reversibility of changes in optical properties after subsequent reducing and oxidizing annealing, allows making an assumption that oxygen diffusion plays a crucial role in coloration/discoloration of LiNbO₃.

Comparative X-ray studies showed that the structure of the surface layers corresponds to the LiNb₃O₈ phase, while internal surfaces retain the structure of LiNbO₃. This can be explained by the partial loss of Li-ions from the crystal surface layers during their reducing thermal treatment.

The AA spectra observed in reduced crystals can be splitted into three bands with maxima in the regions of 350-410, 500-520 and 700-750 nm. The band in 500-520 nm spectral region can be attributed to the absorption of bipolarons, and the band in 700-750 nm spectral region – to the absorption of bound polarons. The absorption of the short-wave band can probably be attributed to the defects in the anion sublattice that captured electrons due to the oxygen loss in the crystal. The difference in nature of the AA bands is confirmed by the differences in their intensity and spectral position depending on the depth, at which the measurements were performed, crystallographic direction and annealing temperature.

The coloration/discoloration processes in crystals are anisotropic – maximal diffusion depth is observed along the Z -direction, minimal – along the X one. This can be explained by the peculiarities of the LiNbO₃ crystal structure, where movement of ions along the Z -direction is facilitated. Experimentally obtained distribution of depth-dependent additional absorption in reduced crystals was successfully approximated basing on the V_O diffusion model and solution of differential equations set describing the quasichemical reaction of bipolarons formation due to the oxygen loss in LN crystal.

The AA maximum on depth-dependent discoloration dependencies after oxidizing annealing of previously reduced LN samples can be explained by two diffusion processes occurring simultaneously in opposite directions – oxygen diffusion from the environment to the crystal and oxygen diffusion from the areas of the crystals, which were not reduced (not colored) after annealing in H₂ at 600 °C.

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